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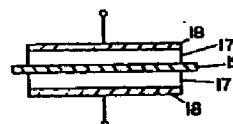
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(54) DOUBLE ELECTRIC LAYER CAPACITOR.

(57) A double electric layer capacitor utilizes double electric layers formed at the boundaries between polarized electrodes and an electrolyte. The polarized electrodes (17) are of carbon or activated carbon fiber, and conductive electrodes (18) are formed as current collectors on the electrode (17) of carbon or activated carbon fiber, thereby forming an electrode unit.

FIG. 8



S P E C I F I C A T I O N

TITLE OF THE INVENTION

ELECTRIC DOUBLE LAYER CAPACITOR

FIELD OF THE TECHNOLOGY

This invention relates to an electric double layer capacitor using activated carbon as polarizable electrode.

BACKGROUND TECHNOLOGY

The electrolytic double layer capacitor is constituted by constituting a polarizable electrode unit by an activated charcoal layer 1 and a collector electrode 2 for that layer, and by putting a separator 3 soaked with an electrolyte between a pair of polarizable electrodes.

Hitherto, as the constitution examples of electrolytic double layer capacitors of this kind, there have been the following two kinds. That is, the first one that is, as shown in FIG. 1, expanded metal or punching metal worked from aluminum sheet is used as collector body, a paste containing activated charcoal powder as main component and a binder of fluorine resin or the like as a polarizable electrode 5 is coated to be held on a surface of the collectors 4 by rolling rollers 7, and a pair of the collectors 4 and the polarizable electrode 5 with a separator 8 inbetween are wound up and electrolyte is injected thereto. FIG. 4 is a sectional structure of the electric double layer capacitor of this system, FIG. 5 is an enlarged view of a part of FIG. 4. 9, 10 are electrode lead, 11 is an outside face, 12 is a rubber sealing cap.

The second one has a structure as shown in FIG. 6, that is, conductive elastomer 13, insulative ring 14, separator 15 and a viscous mixture 16 of activated charcoal powder and an electrolyte are combined as shown in the drawing, and has a disk type outside view as shown in FIG. 7.

Both of these conventional ones use powder type activated charcoal as polarizable electrodes. Therefore they have many problems on characteristics and manufacturing.

In the one of the first type, bonding force between the metal collectors 4 and the polarizable electrode 5 of activated charcoal is weak, and such tendencies are observed that the polarizable electrodes 5 drop off and peel off the collectors 4 or bonding force between both ones becomes weak during use because of strain by the winding up and thereby internal resistance of the electric double layer capacitor gradually increases, to gradually decrease the capacitance. Furthermore, when the polarizable electrode 5 consisting of the activated charcoal powder and the binder are rolled onto the collectors 4, its coating efficiency is bad, and scattering of capacitance due to in uniform coating and rolling of the polarizable electrodes 5 is given as the point to be improved. Furthermore, in conjunction with the structure, that which fulfills needs of known micro-electronics, for instance of flat plate type structure, has been difficult to realize.

In order to dissolve the structural defect, various proposals, for instance, raising contact strength of the polarizable electrodes 5 by roughening by blasting or

the like operation, the surface of the collectors 4, or by strengthening bonding force of the activated charcoal by adding binder such as methyl cellulose to the activated charcoal powder, have been tried, but neither one has satisfactory points yet, though slight improvement of characteristics are observed.

Furthermore, in the one of the second type, though a flat plate type ones are obtainable enabling to respond to minimization of the apparatus, there is a complicated point in working in the manufacture since powder type activated charcoal is used, and furthermore it is not satisfactory also from the view point of capacitance per volume performance.

Presently, though as the electric double layer capacitor of the second constitution the ones using aqueous solution of sulfuric acid as the electrolyte are sold in the market, breakdown voltage per unit cell becomes 0.8 V in this type, and it does not fulfil a demand of high breakdown voltage.

Furthermore, as a modified example of the first type one, an electric double layer capacitor wherein two sheets of carbon fiber are used as polarizable electrodes, and they are wound up in a roll type with a separator inbetween, and about 1 mm step is made on the opposing electrode only at edge face and metal layer is formed by spray method on both end faces to form collectors and lead terminals simultaneously, is devised. In the capacitor of this type, though forming of the end face electrodes become easy, the fundamental structure is the same as the conventional

first type, and obtaining of further small type capacitor structure is difficult.

DISCLOSURE OF THE INVENTION

This invention provides an electric double layer capacitor utilizing an electric double layer formed at the interface between a polarizable electrode and an electrolyte, wherein carbon fibers, activated carbon fibers, or the like are used as the polarizable electrodes, and forming conductive electrodes as collectors such as a metal conductive layer formed by spray method, a conductive paint layer formed by coating of the conductive paint or a metal foil having conductive bond layer or the like on the polarizable electrodes of the carbon fibers or activated carbon fibers; and it is intended to obtain that which has collectors and the polarizable electrodes structure of high mechanical strength, and a large capacitance per unit volume and low internal resistance and leak current.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a structure view showing fundamental structure of an electric double layer capacitor, FIG. 2 is a process view showing substantial part of manufacturing process of the conventional electric double layer capacitor, FIG. 3 is a perspective view showing essential part structure of the conventional electric double layer capacitor, FIG. 4 is a sectional view of a whole structure of the same electric double layer capacitor, FIG. 5 is an enlarged view of a part of FIG. 4, FIG. 6 is an exploded perspective view showing another electric double layer

capacitor, FIG. 7 is a perspective view showing completed state of the same electric double layer capacitor, FIG. 8 is a structure view showing fundamental structure of an electric double layer capacitor in accordance with this invention, FIG. 9 is a front view showing half-part in section of a concrete structure example of an electric double layer capacitor of this invention, FIG. 10 is a construction view showing a second fundamental construction of an electric double layer capacitor of this invention, FIG. 11 is a characteristic chart showing temperature characteristic of capacitance of the conventional electric double layer capacitor, FIG. 12 is a schematic view showing activated carbon-electrolyte interface showing a relation between diameters of micro-pores of the activated carbon and the electric double layer, FIG. 13 is a process chart showing manufacturing process of the activated carbon fiber, FIG. 14 is a characteristic chart showing a relation between activation process of the activated carbon and pore size distribution, FIG. 15 is a structure view showing another example of electric double layer capacitor of the present invention, FIG. 16 is an equivalent circuit diagram of resistance of electric double layer capacitor, FIG. 17 is an enlarged view of an activated carbon cloth, FIG. 18 is an enlarged view showing positional relation between activated carbon fiber and conductive electrode in a polarizable electrode, FIG. 19, A and B are enlarged views showing micro-structures of activated carbon fibers for use in electric double layer capacitor of the present

invention, FIG. 20 is an enlarged view showing collector structure of an electric double layer capacitor of the present invention, FIG. 21 is a schematic view showing pores of activated carbon fiber of high specific surface area, FIG. 22 and FIG. 23 are characteristic graphs showing relation between specific surface area of the activated carbon and capacitance taking out efficiency of electric double layer, FIG. 24 and FIG. 25 are sectional views showing structural example of laminated type electric double layer capacitor of the present invention, FIG. 26, A and B are sectional views showing method of forming end face electrodes of laminated type electric double layer capacitor, FIG. 27 through FIG. 30 are perspective views and a sectional view showing an embodiment of laminated type electric double layer capacitor, FIG. 31, A—D are process chart showing manufacturing process of a coin type electric double layer capacitor of the present invention, FIG. 32 is a characteristic graph showing temperature characteristic of a capacitance of an electric double layer capacitor of the present invention, FIG. 33 is a perspective view of an essential part showing another embodiment of electric double layer capacitor of the present invention, FIG. 34 is a sectional view showing completed state of the same capacitor.

BEST MODE FOR EMBODYING THE INVENTION

Concrete contents of the present invention are explained in accordance with FIG. 8—FIG. 34.

FIG. 8 shows fundamental construction of electric double layer capacitor in accordance with this invention; in FIG. 8, 17 is a polarizable electrode consisting of a cloth, a paper, a felt and so on consisting of carbon fiber and activated carbon fiber, 18 is a conductive electrode formed on the polarizable electrode 17. One pair of the polarizable electrode 17 comprising the conductive electrode 18 are disposed to oppose each other with electrolyte-soaked separator 19 inbetween.

FIG. 9 is a view showing representative example of outside forming of the electric double layer capacitor of this invention. Capacitor element comprised of polarizable electrodes 17 made of activated carbon cloth, conductive electrodes 18 and a separator 19 is enclosed in a pair of metal cases 20 making a pair with two pieces, to form a coin type. 21 is an insulative gasket ring for carrying out insulation and sealing between the metal cases 20, and with this insulative gasket ring 21 inbetween the pair of metal cases 20 are connected. That is, each of the conductive electrodes 18 formed on the polarizable electrodes 17 electrically contacts the inside face of each of the metal cases 20, and in this embodiment the metal cases 20 become electrodes for output taking out.

In FIG. 10, another embodiment of this invention is shown. In this embodiment, polarizable electrodes are constituted by activated carbon fiber 23 carrying electric conductivity improving agent 22 such as conductive paint for raising conductivity. Incidentally, the conductivity

improving agent 22 may be provided on the activated carbon fiber 23 not only on the face of the side of the conductive electrode 18 but also to the other face and on whole body.

Nextly, the characteristic and contents are described in detail individually on respective component elements of the electric double layer capacitor of this invention.

(1) Polarizable Electrode

Properties demanded when activated carbon fibers or carbon fibers are used as the polarizable electrode are:

① surface area per unit weight is large, ② electric resistance is small, ③ mechanical strength is high, ④ resistivity against chemicals is high. Conventional activated carbon powder has the properties of ①, ② and ④, but the activated carbon powder and carbon fiber have, in addition to the above-mentioned, a mechanical strength as electrodes ③ and is very effective material. Activated carbon fiber fulfilling such demand comprises four kinds, phenol kind (cured novolak fibers), rayon kind, acryl kind and pitch kind. Table 1 shows properties of these four kinds activated carbon and coconut-granule activated charcoal.

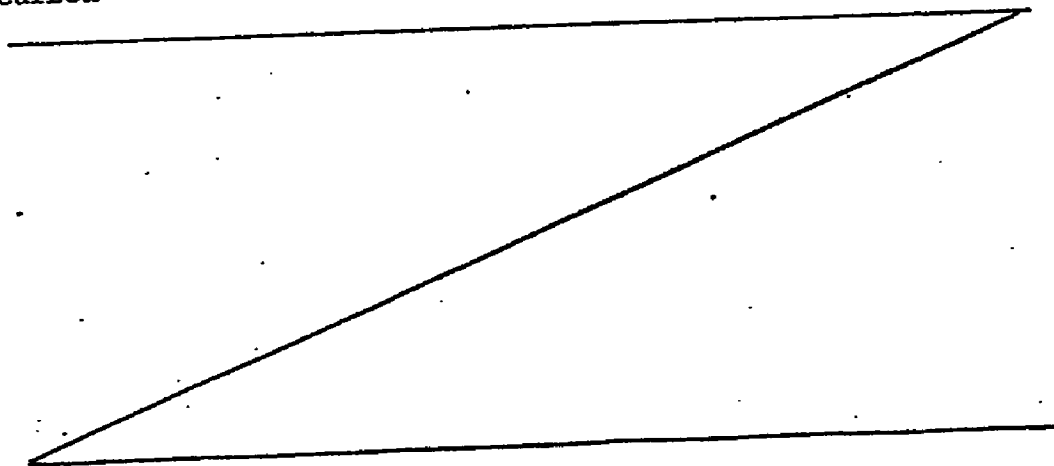


Table 1

	Phenol	Rayon	Acryl	Pitch	Coconut granule charcoal
Surface area (m^2/g)	1500—2000	1400	900	700	800
Tensile strengths (Kg/mm^2)	50—70	5—10	200—250	60	-----
Tensile modulus of elasticity (Kg/mm^2)	2000—3000	1000—2000	2000—3000	3000—3500	-----
Specific electric resistance ($\times 10^{-5} \Omega\text{-cm}$)	1000—3000	2000—3000	800—1000	2000—3000	-----
Electrode types	Felt type, mat type	Possible	Possible	Possible	Impossible
	Cloth type (plane, twilled)	Impossible	Impossible	Impossible	Impossible
	Paper type	Possible	Impossible	Impossible	Possible
Principal properties of carbon fibers as polarizable electrode	Strong and flexible, most suitable as electrode	Hard and relatively fragile	Hard and relatively fragile, but in better than coconut granule charcoal	Hard and relatively fragile, but in better than coconut granule charcoal	To make a thin type electrode a collector is necessary and hence, capacitance is very small

As shown in Table 1, acryl kind and pitch kind generally somewhat lacks flexibility, and specific surface area is fairly small. Though rayon kind has large specific surface area, its fiber is fragile; and though the felt type carbon fiber is popular, it is difficult to be made paper, and paper type is impossible, and it has problems in resistivity against chemicals and resistivity against water. On the other hand, the phenol kind carbon fibers utilize cured novolak fibers as material, and in the case of the phenol kind carbon fibers, because the cured novolak fibers are insoluble and has small heat shrinkage, there is no need of preliminarily making the material fiber insoluble, and the woven or non-woven cloth can be made into the activated carbon as they are, and besides they are strong and superior in flexibility, and therefore they are especially superior as polarizable electrodes of electric double layer capacitor.

It is observed that making of papers from phenol kind carbon fibers as material has various advantages, and especially the ones made by using special Kynol (merchandise name of phenol kind carbon fibers from Nippon Kynol Inc.) as material has superior characteristic in various aspect such as flexibility, electric resistance, water resistivity, chemical resistivity, strength against winding working, working accuracy, electric capacitance, cost and so on.

Nextly, description is made on structure of micropores of activated carbon fibers most suitable for polarizable electrode of electric double layer capacitor.

Activated charcoal which hitherto has been used as polarizable electrode of electric double layer capacitor has specific surface area of 300—3000 m²/gr, and when considering that the electric double layer capacitance, in case mercury is used as polarizable electrode is 20—40 μF/cm², a large capacitance or 60—1200 F per 1 gr of the activated charcoal must be obtainable in theory. However, in the conventional electric double layer capacitor, capacitance per unit weight of the activated charcoal has been taken out only 1/30—1/10 of the above-mentioned theoretical value.

Furthermore, when temperature characteristic of the stored capacitance of the electric double layer capacitor is noted, especially in case of the capacitors wherein surface area utilization factor is bad, temperature dependency of the capacitance change rate ΔC becomes very large as shown in FIG. 11, resulting in what is called electric double layer capacitor of bad temperature characteristic.

Such poorness of utilization factor of the area of the activated charcoal and poorness of temperature dependency induced thereby is considered as being induced by distribution of diameter of micro-pores of the activated charcoal used, as below-mentioned. FIG. 12 is a schematic chart of electric double layer formed on surface of the activated charcoal, and when an electric field is applied between the activated charcoal substrate 24 and electrolyte 25 contacting thereto, an electric charge is stored at the surface of the activated charcoal substrate 24, and the depth of the interface electric double layer is about

10 Å. Accordingly, as shown in FIG. 12, in a micro-pore 26 having a diameter larger than $10 \times 2 = 20$ Å, the electric double layer is formed up to the inside of the micro-pore 26 and the electric double layer capacitance is stored up to the inside surface of the micro-pore 26, while for micro-pore 27 of 20 Å or smaller no electric double layer is formed between its inside wall and the electrolyte. In other words, no matter how ones having specific surface area per unit weight is induced by micro-pores of diameter of 20 Å or smaller is used as the polarizable electrode, the utilization factor of the surface area becomes very bad.

Furthermore, when temperature characteristics of the easiness of diffusion of the electrolyte into the micro-pores and thickness of the electric double layer are considered, it is understood that temperature dependency of the electric double layer capacitance formed on the surface of the activated charcoal having many micro-pores of small diameter becomes very large, as compared with that of the activated charcoal having micro-pores of large inner diameters as major proportion.

By considering the above, structure of the micro-pores of the activated carbon fibers required as the polarizable electrode is that specific surface area is large and besides there are many micro-pores having diameters of 20 Å or larger. Nextly, manufacturing method of the activated carbon fiber having such micro-pores structure is described.

FIG. 13 is manufacturing process diagram of a general activated carbon fibers. That is, there are a method that material fibers are directly made carbonized and activated, and a method that once carbon fiber is made and subsequently activated. Such activation of the carbon fibers (steps A and B in FIG. 11) is carried out in general in a mixed gas consisting of water vapor and nitrogen at a temperature of 700°C—800°C. Thereupon, when metal ions are co-existed in the material fiber during such activation, the diameter of the micro-pores of the activated carbon fibers after activation can be controlled. That is, as compared with the case activated by the water vapor only, micro-pores having inner diameters proportional to the diameters of metal ions used as catalyst are formed. Metal ions suitable for coexistence are of lythium, sodium, potassium, calcium, magnesium, zinc and so on, and when metal ions of the larger ion radius are used as catalyst, the micro-pores of the larger diameters are obtainable. Actually, salts (chlorides, phosphates, nitrates, etc.) or hydroxides of these metal ions are carried on the material fiber, to activate.

FIG. 14 shows pore size distribution of activated carbon fibers after activation, drawn individually of each catalyst used, and as is shown, especially when salts or hydroxides of the alkali earth metals are used as the activation catalyst, distribution rate of the micro-pores of diameter above 20 Å becomes large.

Furthermore, specific surface area is in inverse proportional relation to electric resistance and softness, and as the activation is done the surface area increases, carbonization yield decreases, resistance increases and it mechanically becomes fragile. In the fibers wherein the micro-pores of 20 Å or smaller is of majority and surface area utilization factor is bad, the activation must proceed until a large specific surface area is obtained, then even though a satisfactory value as the capacitance value is obtained as a result, it makes a polarizable electrode with high resistance and weak mechanical strength. However, in case the activation catalyst is used like the present invention, the surface area utilization factor very much improves, and hence there is no need of advancing the activation extremely to obtain a unit capacitance, and the activated carbon cloth obtained in this way as such has low resistance and high strength. Furthermore, since the activated carbon fiber has low resistance and large diameter of the micro-pores, it has a feature that the internal resistance of the capacitor becomes very low.

As is described below, when considering to provide the polarizable electrode by die-cutting of the activated carbon cloth, that mechanical strength of the activated carbon cloth becomes strong means that the manufacturing process becomes easy, and the activated carbon cloth of the present invention is very much advantageous in manufacturing process, too.

Furthermore, with respect to the ratio of the micro-pores of the diameter of 20 \AA or more to the whole micro-pores, when the total of the inside-surface area of the micro-pores is less than 1% of the total inside-surface area of the whole micro-pores, its special effect can not be expected much, and in case the inside-surface area of the micro-pores of the inside diameter of 20 \AA or more becomes 1% or more its effect becomes prominent.

(2) Conductive Electrode .

Conductive electrodes used in this invention is conductive layers formed on the polarizable electrode directly by plasma spraying, arc spraying, vacuum deposition, sputtering, non-electrolytic plating, etc. Furthermore, metal foil with conductive bond inbetween or conductive paint is suitable as the electrodes. Specially for its strength, conductivity and easiness of forming, metal layer formed by the plasma spray or arc spray method or metal foil with conductive bond inbetween is suitable as the electrodes.

Firstly, electrodes by the spray method is described. As conductive material used here, aluminum, nickel, copper, zinc, tin, lead, titanium, tantalum, and the like which are electro-chemically stable against electrolyte. Deposition weight by the spraying of 0.05 mgr/cm^2 — 500 mgr/cm^2 is appropriate. In the case by other deposition method, this is not applicable. In the spray method, under this range, electric resistance is

high and function as electrodes is not performed. Furthermore, above this range, the electrodes become too thick, and is likely to peel off or drop out from the carbon fibers, or forming cracks in the spray metal layer, and mechanical strength becomes weak oppositely. That is, polarizable carbon fiber electrodes having appropriate amount of collected sprayed layer comprises such mechanical strength and proper characteristic of the activated carbon, and besides in comparison with the case by the conventional paste method, handling in manufacturing is very easy, and resultantly, as will be described in the below-mentioned embodiment, coin type flat sheet-shaped electric double layer capacitor is obtainable.

As the conductive electrodes, besides such metal layer formed by the spray method, a method shown by FIG. 15 is possible. That is, it is an electrode structure, wherein, on polarizable electrode 17 made of activated carbon fiber, a metal foils 29 of the same material as the sprayed metal, is provided with a conductive binder 28, for instance what is made by dispersing carbon, silver or copper in an organic resin such as epoxy resin, phenol resin, acryl resin, silicone resin, and so on.

Conductive electrodes of these structure also, in case of application in the electric double layer capacitor of, for instance, coin type flat sheet shape, electrically contact the conductive electrodes as will be described in the below-mentioned embodiment.

Furthermore, as the conductive electrodes, they may be formed by applying conductive paint having

conductive pulverized powders of silver, copper, carbon, or the like dispersed in organic resin.

Nextly, another large characteristic with respect to the conductive electrodes is described. FIG. 10 is a drawing to show fundamental structure of electric double layer capacitor of the present invention comprising electric conductivity improving agent 22, wherein when attention is paid on the internal resistance of the capacitor, with respect to a capacitor of a structure shown in FIG. 8 its internal resistance is divided into individual components as in FIG. 16. That is, these are contact resistance R_1 between the conductive electrode 18 and a polarizable electrode 17, resistance R_2 in the polarizable electrode 17 and interface resistance R_3 between the polarizable electrode 17 and an electrolyte impregnating in the separator 19, a resistance R_4 of the electrolyte and R'_3 , R'_2 and R'_1 which exist in symmetry to these ones. Those using the carbon fiber as the polarizable electrode as this invention, as shown in FIG. 17, since such cloth that as the activated carbon fibers 30, each other entangled in diagonal or plain fabric is used, density of the carbon fiber per unit area of the cloth becomes low. Accordingly, as compared with a one with polarizable electrodes using powder activated carbon type, resistances become large in every direction, thicknesswise and in planewise. Furthermore, though it can not be denied that leading of the electric double layer capacitance of the interface between the polarizable electrode 17 at the micro-pores parts 31 of the activated

carbon fiber and the electrolyte 32, to the conductive electrode 18, by relying on a conductivity only by the activated carbon fiber 33 and by contacts and connections between them, results in making the R_2 and R'_2 high resistances. However, the problem on these internal resistances become prominent in the coin type capacitors having small polarizable electrode area.

From these view points, when the surface of the polarizable electrode as shown in FIG. 10 is shown by enlarging, it becomes as of A and B of FIG. 19. As shown in A of the same figure, conductivity improving agent 22 is born on all the surface of the activated carbon fiber 33, and as shown in FIG. B the micro-pore parts 34 of the activated carbon fibers are also coated by the conductivity improving agent 22.

As the conductivity improving agent to be used here, three kinds are considered: ① oxides of transition metals such as ruthenium, osmium, iridium, indium, platinum, etc., ② conductive paint made by dispersing carbon granules or other metal granules in organic resin or carboxy methyl cellulose or the like, ③ conductive metal layer of tin oxide or indium oxide formed by vapor deposition, sputtering or the like. At the interface between the polarizable electrode and the electrolyte, it is an essential condition that only a reaction to form the electric double layer takes place, and when chemical and electric stability of the polarizable electrode are considered, uses of these stable oxide of conductive

transfer metals or conductive paint or furthermore, conductive oxide such as tin oxide, as the conductivity improving agent.

Furthermore, when, for instance, the activated carbon fibers are dipped in an aqueous solution of ruthenium chloride for a predetermined time and the above is thermally decomposed by keeping the aqueous solution of ruthenium chloride sufficiently soaking in the micro-pores in the activated carbon fiber, a layer of ruthenium oxide is coated to the inner wall of the micro-pores even to the extremely microscopic ones of the activated carbon fibers.

By using the polarizable electrode of the activated carbon fiber 33 having such conductivity improving agent 22 on its surface, as is understood from comparison between, for instance, resistance $10^{-1} \Omega \cdot \text{cm}$ — $10 \Omega \cdot \text{cm}$ of the activated carbon fibers and resistance $10^{-5} \Omega \cdot \text{cm}$ of ruthenium oxide, low resistance layer becomes to be formed on the surface of the activated carbon fibers 33, and as shown in FIG. 20, electric double layer.. formed on the inside surface of the activated carbon fibers 33 is connected with low resistance to the conductive electrode 18 through conductivity improving agent 22 formed on the surface.

As a result, resistance R_2 in the above-mentioned polarizable electrode, namely the resistance in the activated carbon fibers, furthermore the contact resistance R_3 between the polarizable electrode and the electrolyte or contact resistance R_1 between the polarizable electrode and the collector electrode becomes also small, and internal

resistance of the electric double layer capacitor can be very much decreased.

Furthermore, as above-mentioned, in case the conductivity improving agent is formed by using a thermally decomposable salt such as ruthenium salt, electrode lead out of the micro-pores of activated carbon fibers can be easily made, and accordingly surface area utilization factor of this part is also increased.

Besides, forming methods of the conductivity improving agent to be used in this invention are as follows: (1) dipping and thermal decomposition of thermally decomposable salt such as ruthenium chloride, (2) painting or dipping method of carbon colloid solution, (3) forming by vacuum deposition of conductive oxide such as tin oxide. When formation of the conductivity improving agent in the micro-pores of the activated carbon is considered, the method of (3) is disadvantageous, but when contemplating kinds and heat resistivity of the activated carbon fiber to be used, any of the method (1), (2), (3), has respective features, and can achieve more superior characteristics than the electric double layer capacitor not provided with the conductivity improving agent.

(3) Electrolyte

The electrolyte to be used in this invention comprises as its one component thereof, at least 1,2-dimethoxyethane.

As electrolytes for conventional electric double layer capacitor shown in FIG. 4 and FIG. 5, by considering

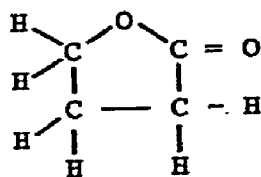
permeability, conductivity, chemical and thermal stability, that which is made by dissolving tetramethylammonium-perchlorate, ammoniumperchlorate or the like in solvent such as propylene carbonate, dimethylformamide, γ -butyrolactone, or tetrahydrofuran or the like have been used. However, with such combination of the conventional electrolyte and activated charcoal, due to low permeability of the electrolyte to the activated charcoal and high viscosity, impregnation of the electrolyte into the pores of the activated charcoal is not completely done, and this becomes the reason to hinder effective utilization of the surface area like the case of the aforementioned distribution characteristic of the micro-pores of the activated carbon fibers.

FIG. 21 is a view showing micro-structure of the activated carbon fiber of phenol kind. Among the micro-pores 35 of the activated carbon fibers, the micro-pores to contribute formation of the electric double layer is the micro-pores of cylindrical shape with diameters of several tens \AA —several μm , and in order to effectively utilize the surface area of this micro-pores an electrolyte which can reach through at least the micro-pores of the diameter of several tens \AA —several μm to the bottom 36 of the micro-pores 35.

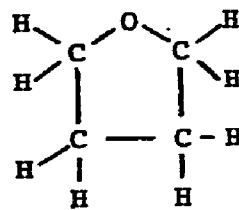
1,2-dimethoxyethane to be used in this invention is a dimethylether of ethylene glycol, and dissolves in the water, alcohol and hydrocarbon, but is a stable liquid having the boiling point at 82°C — 83°C . γ -butyrolactone, tetrahydrofuran, dimethylformamide or propylene carbonate which has been

hitherto used as solvent for electrolyte of electric double layer capacitor has poor permeability into the micro-pores because of its molecular radius or three dimensional hindrance due to having carbonyl group, amino group with methyl group or cyclic construction. In contrast to that, the 1,2-dimethoxyethane are of low molecular number and has ether structure, hence substantially of straight chain type. Accordingly, the permeability into the micro-pore is superior than the conventional ones, and especially is effective in effective utilization of the surface area of the activated carbon fibers having cylindrical type micro-pores as above-mentioned.

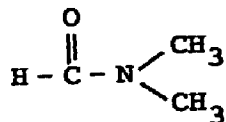
(γ-butyrolactone)



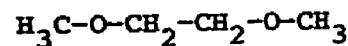
(tetrahydrofuran)



(dimethylformamide)



(1,2-dimethoxyethane)



Nextly, the effect of combination of 1,2-dimethoxyethane and activated carbon fiber of relatively large surface area is described in concrete.

FIG. 22 shows capacitance efficiency (the capacitance efficiency to be referred to here is a value when considering only such micro-pores that has possibility of contributing to formation of electric double layers) which is to be

taken out when activated carbon fibers of three types of specific surface areas ($1000 \text{ m}^2/\text{gr}$, $1500 \text{ m}^2/\text{gr}$ and $2000 \text{ m}^2/\text{gr}$) are used as polarizable electrodes, with respect to the case "a" where propylene carbonate is used as electrolyte solvent, the case "b" where both 1,2-dimethoxyethane and propylene carbonate are used in this invention. From FIG. 22, it is understood that when propylene carbonate is used as electrolyte solvent, even when the specific surface area of the polarizable electrode is increased from $1000 \text{ m}^2/\text{gr}$ to $2000 \text{ m}^2/\text{gr}$, capacitance value does not substantially increase, or even decreases. In contrast to this, when 1,2-dimethoxyethane is used also as the electrolyte solvent, when the specific surface area of the activated carbon fiber increases the capacitance value also increases in proportion thereto, and ratio of the capacitance of the case using the activated carbon of $1000 \text{ m}^2/\text{gr}$ and that of the case using the activated carbon of $2000 \text{ m}^2/\text{gr}$ is about 1 : 2.

FIG. 23 shows a relation between the surface area and capacitance efficiency when coconut activated charcoal powders ($300 \text{ m}^2/\text{gr}$, $500 \text{ m}^2/\text{gr}$ and $700 \text{ m}^2/\text{gr}$) are used as the polarizable electrodes and propylene carbonate is used as the electrolyte. That is, when a low surface area material as the coconut activated charcoal granules used as the polarizable electrode, even in the case "a" when propylene carbonate is used as the electrolyte solvent it fairly serves the function. Also, as shown by the characteristic "b", even in case the low surface area material is used as the polarizable electrode, the effect of 1,2-

dimethoxyethane is obtainable. These experimental facts support the consideration on the above-mentioned relation about the shape of micro-pores of activated carbon fibers of high specific surface area, and permeability of the electrolyte against efficiency for taking out capacitance; and use of 1,2-dimethoxyethane as the electrolyte solvent is desirable.

As a means for further making the effect of the 1,2-dimethoxyethane more prominent, a use of vacuum impregnation method in permeating electrolyte into the activated carbon fiber is also an effective means. Furthermore, after forming conductive electrodes as cathode collector on graphite fibers of novolak group by a means such as plasma spraying, an electrolyte containing a solvent consisting of propylene carbonate and 1,2-dimethoxyethane by the vacuum diffusion method is also effective.

Nextly, laminated type capacitor wherein plural number of hitherto-described unit capacitor elements are laminated and metal-sprayed layer is formed on the end face to take out the whole electrodes. Capacitors of such structure is classified into the following two types. That is, they are a first type having unit capacitor element of a combination of polarizable electrodes and a separator, and a second type having a unit capacitor element of a combination of one polarizable electrode, one separator and one non-polarizable electrode.

FIG. 24 shows fundamental structure drawing of the first type one.

A polarizable electrodes 37 consisting of cloth, paper or felt of carbon fibers or activated carbon fibers, conductive electrode 38 formed on one side of the polarizable electrode 37 and a separator 39 soaked with electrolyte and disposed between the polarizable electrodes 37 constitute a composition which forms a unit capacitor element 40. In the unit capacitor element 40, the polarizable electrodes 37 are disposed in a manner to form margin part 40a whereat conductive electrodes 38 do not face each other. At this time, the conductive electrodes 38 functions as the collector electrode. n pieces of the unit capacitor elements 40 are, alternatively laminated as shown in FIG. 24, and metal layers 41, 42 are provided on both ends of the laminated body to form collected electrodes for outside leading out. At this time, it is more preferable to make insulation between neighboring unit capacitor elements 40 by putting an insulation spacer 43 or the like inbetween.

FIG. 25 shows fundamental structure drawing of the second type one.

A combination body of polarizable electrodes 37 consisting of fabric, paper or felt of carbon fibers or activated carbon fibers and separators 39 soaked with electrolyte constitute a unitary capacitor element 44; and in this unitary capacitor element, in the polarizable electrodes 37 which are opposing with the separator 39 inbetween, the conductive electrode 38 having one polarizable electrode 37 formed thereon is disposed to the side of the separator 39. The unit capacitors 44 are as shown in FIG. 25, laminated of their n pieces with

separator 39 inbetween and on both sides of this laminated body, metal layers 41 and 42 are provided. Furthermore, also, in the unit capacitor element 44, margin parts 44a, whereat conductive electrodes 38 of the polarizable electrodes 37 do not oppose each other, are provided on both ends.

In the electric double layer capacitor of this structure, the conductive electrodes 38 function as collector electrodes, and the conductive electrodes 38 contacting the separator 39 functions as non-polarizable electrodes, thereby constituting respective unit capacitor elements.

Nextly, electrode lead out of such laminated capacitor is described. As has been described, for leading out end faces of the collector electrodes of unit capacitor group, two metal layers for electrodes of the whole capacitor exist. These metal layers are formed in a manner that, for every other capacitor elements, electrode leading-outs are formed on the same side, and it is necessary to be formed in a manner that electrodes of the neighboring unit capacitor elements do not contact each other.

As a means to achieve this purpose, it is desirable to form the collector electrodes by plasma spraying method or the like. A and B of FIG. 26 are cases of spraying metal powder 47 onto the main body 45 consisting of laminated unit capacitor element group by using spraying gun 46. In this time, insulation spacers 43 may be provided in order that electrodes 48 and 49 of the neighboring unit capacitor elements do not make conduction. And in FIG. 25b, only electrodes designated by the hatching of the same

direction are made contact with the sprayed electrodes 50. FIG. 27—FIG. 30 show an example of completed state of this laminated type capacitor, and making in face bonding type as shown in FIG. 27 or making in that metal lead wires 51 are disposed on both end faces of the main body 45 of the capacitor when sprayed electrode 50 is formed to be buried in the sprayed electrodes, or made in a manner that after forming the sprayed electrode 50 as shown in FIG. 29, metal lead wires 51 are connected to the metal deposited electrodes 50 by silver paint or solder 52, can be considered. Covering is made for all of these by encapsulating the whole body into a case of resin, metal or ceramic, or dipping in the resin.

One example when the outside forming is made by case is shown in FIG. 30, and in this example lead pieces 55, 56 are spot-welded on the inside face of two metal cases 53, 54 of disk shape, and the metal cases 53 and 54 are combined in a manner that the capacitor main body 45 is encircled therewith and respective lead pieces 55, 56 of the metal cases 53, 54 are electrically connected to the sprayed electrodes 50 of the capacitor main body. 57 are insulation spacers to prevent direct contacting of the sprayed electrodes 50 of the main body 45 of the capacitor to the metal cases 53, 54; and 58 is a gasket for preventing contacting of the metal cases 53, 54 to each other.

Nextly, concrete embodiments of the present invention are described.

(Embodiment 1)

As shown in A—D of FIG. 31, on each surface of polarizable electrodes 59 consisting of cloth made of activated carbon fibers of phenol kind (thickness 0.3 mm, specific surface area $2000 \text{ m}^2/\text{gr}$) and a cloth made of activated carbon fibers of acryl kind (thickness 0.3 mm, specific surface area $800 \text{ m}^2/\text{gr}$), an aluminum layer 60 of thickness $5 \text{ }\mu\text{m}$ is formed by plasma spraying method. This double layer structure 61 is die-cut into disks having 2 cm diameter to provide electrode body 62. After soaking in the electrode bodies 62 an electrolyte of a mixed solution of propylene carbonate 30 wt % and γ -butyrolactone 70 wt % with addition of 10 wt % of tetraethylammoniumperchlorate, laminating a separator 63 inbetween and further, pinching it with two cases 64 of stainless steel, and disposing a gasket 65 at the opening end of the cases 64 and also caulking are made to seal.

Several characteristics of electric double layer capacitor in accordance with this invention are shown in Table 2. Table 2 also shows characteristics of trially made product of the same shape as the structure of FIG. 4 wherein activated charcoal paste is coated on the punching metal collector body and the structure of FIG. 6, for the sake of comparison.

Table 2

	Activated /carbon charcoal used	Capacitance	Internal resistance	With-stand voltage	High temperature load life at 1.7V, 70°C, 1000/hr.
Product of the present invention	Activated carbon fiber of phenol group	3 F	0.15 Ω	2 V	(Capacitance change) -3 %
	Activated carbon fiber of acryl group	1.5 F	0.15 Ω	2 V	-3 %
Conventional product	Paste of activated charcoal powder applied on aluminum expanded metal	0.8 F	0.3 Ω	2 V	-20 %
	Activated charcoal powder with sulfuric acid	0.8 F	0.1	0.8 V	-20 %

(Embodiment 2)

In a cloth of phenolic fibers, aqueous solution of zinc chloride is soaked to be born. At this time, the amount of born NaOH is made to be 10 % of the whole fiber weight. The fiber thus treated is kept in a furnace of 1000°C, to be carbonized and activated. By controlling the time of retention in the furnace, activated carbon fiber cloths of three kinds of specific surface areas of 300 m²/gm (30 min. retention), 500 m²/gr (1.5 hrs. retention) and 1500 m²/gm (3 hrs. retention) are obtained. Furthermore, aluminum metal layer of 50 μ m thickness is formed by plasma spray method and thereafter is die-cut into circle-shaped ones of 5 mm diameter. On this circle-shaped electrode body, electrolyte of mixed solvent of propylene carbonate 30 wt % and γ -butyllactone

70 wt % with addition of 10 wt % tetraethylammoniumperchlorate is soaked, and putting a separator made of polypropylene between two sheets of the electrodes, outside forming is made by using the cases of stainless steel and gasket.

Table 3 shows characteristics of an electric double layer capacitor of this embodiment. Incidentally, characteristics of electric double layer capacitor using an activated carbon cloth, activated without using the activation catalyst are also described for comparison in the same table. Furthermore, FIG. 32 shows temperature characteristic (-25°C , 25°C and 70°C) of values of capacitance change rates ΔC of the ones using the activated carbon cloth of specific surface area $500 \text{ m}^2/\text{gr}$ among the cases of both.

Table 3

	Property of activated carbon cloth			Characteristics of electric double layer capacitor	
	Specific surface area by BET	Strength	Proportion of micro-pores of diameter over 20 \AA	Capacitance	Internal resistance
Product of the invention	$300 \text{ m}^2/\text{gr}$	Strong	50 %	8 F	1 Ω
	$500 \text{ m}^2/\text{gr}$	Strong	50 %	8 F	1 Ω
	$1500 \text{ m}^2/\text{gr}$	Strong	80 %	10 F	1 Ω
Comparison example	$300 \text{ m}^2/\text{gr}$	Strong	Below 1 %	0.01 F	8 Ω
	$500 \text{ m}^2/\text{gr}$	Weak	Below 1 %	0.05 F	8 Ω
	$1500 \text{ m}^2/\text{gr}$	Weak	Below 1 %	0.2 F	10 Ω

(Embodiment 3)

Cloth of activated carbon of thickness 0.2 mm woven by activated carbon fibers of novolak kind is dipped in aqueous solution of ruthenium chloride of 0.5 mole/l for 5 min., and thereafter is retained in a furnace of 300°C to coat the surface of activated carbon fiber by ruthenium oxide layer. After forming aluminum layer (20 μ m thickness) by plasma spraying method on thus formed cloth of the carbon fibers, it is die-cut into circle-shape with diameter of 20 mm. Between two sheets of this circle-shaped electrodes, a separator made of polypropylene is put and they are laminated, and as electrolyte mixed solution of propylene carbonate, γ -butyrolactone and tetraethylammoniumperchlorate is injected, and they are encapsulated in metal cases with gasket inbetween.

(Embodiment 4)

Cloth of activated carbon of thickness 0.2 mm woven with activated carbon fibers of novolak kind is dipped into a colloidal carbon liquid (Aquadac made by Acheson & Co. of USA), and after being taken out, is dried at 100°C for 10 min. On one side of activated carbon fiber cloth thus made, aluminum layer (thickness 20 μ m) is formed by plasma spray method, and thereafter it is die-cut into circle shape to constitute electrode bodies. Between this circle-shaped electrode bodies, separator made of polypropylene is put and two sheets of the electrode bodies are laminated, and as electrolyte a mixed liquid of propylene carbonate, tetraethylammoniumperchlorate and γ -butyrolactone is injected, and subsequently outside forming

is made by a gasket and metal cases.

(Embodiment 5)

Tin oxide layer (thickness 5 μm) is formed by vacuum deposition method on an activated carbon cloth of thickness 0.2 mm woven with activated carbon fibers of novolak kind. Furthermore, an aluminum layer (20 μm thickness) is formed thereon, and thereafter it is cut into circle shape of diameter 20 mm to constitute electrode body. By putting a separator made of polypropylene between the electrode bodies, two sheets of the electrode bodies are laminated, and as electrolyte a mixed liquid of propylene carbonate and tetraethylammoniumperchlorate is injected and outside forming is made with a gasket and metal cases.

(Embodiment 6)

Activated carbon cloth of thickness 0.2 mm woven with activated carbon fibers of novolak kind is dipped in aqueous solution (0.5 mole/l) of ruthenium chloride for 5 min. Next, it is held in a thermal decomposition furnace of 300°C for 10 min., to form ruthenium oxide layer on a surface of the activated carbon fiber. On one face of the matter thus made, an aluminum layer (thickness 20 μm) is formed by plasma spraying method, it is cut into squares of 3 cm x 3cm to produce electrode bodies. As shown in FIG. 33, these electrode bodies are laminated with separators made of polypropylene put inbetween, and thereafter wound to constitute a cylindrical capacitor body, and the capacitor body is enclosed in a cylindrical case of aluminium, and the opening part of the case is sealed with a rubber cap.

In FIG. 33 and FIG. 34, 66 is electrode body, 67 is aluminum layer, 68 is separator, 69 is lead wire, 70 is capacitor body, 71 is case and 72 is rubber cap.

Several characteristics of the electric double layer capacitor of this invention obtained by the Embodiment 3—Embodiment 6 are shown in Table 4. Furthermore, characteristics of those of button type which is not provided with conductivity improving agent and those of wound up type capacitor are also shown.

Table 4

		Capacitance	Internal resistance	High temperature load life 1.7 V, 70°C, 100 hr.
Products of the invention	Embodiment 3	3.5 F	0.05 Ω	(Capacitance change) -3 %
	Embodiment 4	3.5 F	0.05 Ω	-3 %
	Embodiment 5	3.2 F	0.1 Ω	-3 %
	Embodiment 6	5.2 F	0.01 Ω	-3 %
Comparison example	Button type	3.0 F	0.2 Ω	-5 %
	Wound-up type	4.5 F	0.05 Ω	-5 %

(Embodiment 7)

On one surface of activated carbon fiber cloth of diameter 2.0 cm (of Japan Kynol Inc.) specific surface area 2000 m²/gr) aluminum conductive layer of thickness 5 μ m is formed by plasma spray method.

In this activated carbon fiber cloth, a solution prepared by mixing 1,2-dimethoxyethane 30 wt%, γ -butyrolactone 50 wt% and tetramethylammoniumperchlorate 20 wt% is soaked. This two sheets of the activated carbon fiber cloths are laminated by putting a film of polypropylene of thickness $10 \mu\text{m}$ inbetween, and outside forming was made by outside case made of metal and a gasket made of rubber. Also a sample which is trially made by soaking electrolyte in two sheets of the activated carbon fiber in a reduced pressure atmosphere of 1 mmHg of room temperature retaining for 10 min. was made. A trial making with respect to a capacitor using as electrolyte constituted with propylene carbonate 30 wt%, γ -butyrolactone 50 wt% and tetramethylammoniumperchlorate 20 wt% was also made.

Table 5 shows result of this embodiment.

Table 5

		Capacitance	Internal resistance	High temperature load life (at 1.7V, 70°C, 1000 hr.
Product of the present invention	Normal pressure impregnation	3 F	0.15 Ω	(Capacitance change) -3 %
	Vacuum impregnation	3.2 F	0.14 Ω	-3 %
Comparison example	----	1.5 F	0.5 Ω	-3 %

(Embodiment 8)

On one surface of the activated carbon fiber cloth (of Nippon Kynol Inc., specific surface area $2000 \text{ m}^2/\text{gr}$) an

aluminum conductive layer of thickness 5 μm is formed by plasma spraying method. 10 sheets of what is made by cutting this in 10 mm square are laminated with separators as shown in FIG. 24 and FIG. 25. And, the separator used in this embodiment is of polypropylene film of thickness 10 μm , and in the separator and the activated carbon fiber cloth a solution prepared by mixing propylene carbonate 30 wt%, γ -butyrolactone 50 wt% and tetramethylammonium-perchlorate 20 wt% as electrolyte is soaked. On each other opposing end face of such laminated construction, aluminium layers (thickness 10 μm) are formed by plasma spraying method to carry out electrode taking out. Laminated type capacitor thus made is subject to outside forming in a method shown in FIG. 30, and measurement of characteristic was done.

Table 6 shows comparing characteristics of electric double layer capacitor made in accordance with the present embodiment and conventional capacitor wound by using activated carbon powder in electrodes and a single layer capacitor using activated carbon fiber in electrode.

Table 6

	Capacitance	Internal resistance	High temperature load life (at 1.7V, 70°C, 1000 hr.	Volume ratio
Polarizable electrodes opposing type (FIG. 23)	8 F	0.17 Ω	(Capacitance change) -3 %	1
Polarizable electrode and non-polarizable electrode opposing type (FIG. 24)	8 F	0.17 Ω	-3 %	1
Single layer flat sheet type	2 F	0.15 Ω	-3 %	0.5
Conventional products	8 F	3 Ω	-20 %	10

(Embodiment 9)

On one side of activated carbon fiber cloth of thickness 0.2 mm woven with activated carbon fibers of novolak kind, an aluminium foil of thickness 0.05 mm is bonded with conductive bond of epoxy carbon. Nextly electrode bodies are obtained by die-punching this into circle shape of diameter 20 mm. This circle-shaped electrode bodies are laminated by putting a separator made of polypropylene inbetween, and mixed liquid of propylene carbonate, γ -butyrolactone and tetraethylammoniumperchlorate as electrolyte is injected and outside forming is made with gasket and metal cases.

Characteristics of capacitor thus made is shown in Table 7.

Table 7

Capacitance	Internal resistance	High temperature life test (at 1.7V, 70°C, 1000 hr.)
3.0 F	0.2 Ω	-5 %

POSSIBLE UTILIZATION IN INDUSTRY

As has been explained above, in accordance with electric double layer capacitor of this invention, since polarizable electrodes are constituted with carbon fiber or activated carbon fiber and conductive electrodes are formed on the polarizable electrodes, accordingly such an effect is obtainable as mechanical strength of the electrode parts becomes high,

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and small type capacitors in various shapes are obtainable,
and furthermore capacitance per unit volume can be made
large and besides internal resistance and leak current can
be made low.

WHAT IS CLAIMED IS

1. An electric double layer capacitor utilizing electric double layer formed at an interface between a polarizable electrode and an electrolyte, wherein an element is constituted by forming said polarizable electrode by carbon fibers or activated carbon fibers, forming conductive electrodes on one face of said polarizable electrode and disposing an opposing electrode on the other side of said polarizable electrode with said electrolyte inbetween.
2. An electric double layer capacitor of claim 1, wherein a polarizable electrode consisting of carbon fibers or activated carbon fibers, with a conductive electrode formed on one face thereof, is used as said opposing electrode.
3. An electric double layer capacitor of claim 1, wherein a non-polarizable electrode is used as said opposing electrode.
4. An electric double layer capacitor of claim 1, wherein on one face or on both face of said polarizable electrode, an electric conductivity improving agent for increasing conductivity is carried.
5. An electric double layer capacitor of claim 1, wherein micro-pores are provided in said carbon fibers or activated carbon fibers and it is formed that among the micro-pores, total of the inside surface areas of the micro-pores having inner diameter of 20 \AA or larger occupies 1% or more of the total of the inside surface areas of the whole micro-pores.

6. An electric double layer capacitor of claim 1, wherein carbon fibers of phenol kind is used as said carbon fibers.
7. An electric double layer capacitor of claim 1, wherein activated carbon fibers of novolak kind made by carbonization and activating carbon fibers of phenol kind is used as said carbon fibers.
8. An electric double layer capacitor of claim 1, wherein said polarizable electrode is a cloth, felt or sheet type matter consisting of carbon fibers or activated carbon fibers.
9. An electric double layer capacitor of claim 1, wherein said conductive electrode is constituted by metal layer formed by plasma spraying or arc spraying.
10. An electric double layer capacitor of claim 1, wherein said conductive electrode is made of a metal foil and it is bonded on said polarizable electrode with a conductive bond.
11. An electric double layer capacitor of claim 1, wherein said conductive electrode is formed with a conductive paint.
12. An electric double layer capacitor of claim 1, wherein said electrolyte at least contains 1,2-dimethoxyethane.
13. An electric double layer capacitor of claim 1, wherein said element is enclosed in a pair of metal cases which form a pair with two pieces, and said conductive electrodes on said polarizable electrodes and said opposing electrodes are electrically contacted to said metal cases.

14. An electric double layer capacitor of claim 4, wherein said conductivity improving agent is selected from conductive transition metal oxide, conductive paints and conductive oxides.

15. An electric double layer capacitor of claim 7, wherein carbonization and activation is made by using a metal salt or hydroxide of metal containing ions of lithium, sodium, potassium, magnesium, calcium or zinc as a catalyst.

16. An electric double layer capacitor of claim 9, wherein said sprayed metal is one selected from aluminum, nickel, copper, zinc, tin, lead, titanium and tantalum.

17. An electric double layer capacitor of claim 9, wherein weight of sprayed metal per unit area of said polarizable electrode surface is 0.05 mgr/cm^2 — 500 mgr/cm^2 .

18. An electric double layer capacitor of claim 10, wherein material of said metal foil is one selected from aluminum, nickel, copper, zinc, tin, lead, titanium and tantalum.

19. An electric double layer capacitor of claim 14, wherein said conductive transition metal oxide is selected from ruthenium, osmium, iridium, indium and platinum.

20. An electric double layer capacitor utilizing electric double layer formed at an interface between a polarizable electrode and an electrolyte, wherein said polarizable electrode is formed by carbon fibers or activated carbon fibers having a conductive electrode formed on one face thereof, a unit capacitor element is constituted by laminating this polarizable electrode in a manner

that margin parts are formed on both ends with a separator soaked with electrolyte and put inbetween, and plural number of said unit capacitor elements are laminated and electrodes for outside leading out are formed on both ends of this laminated body.

21. An electric double layer capacitor of claim 20, wherein said unit capacitor element is constituted by disposing one polarizable electrode among polarizable electrodes opposing with said separator inbetween, in a manner that said conductive electrode on said polarizable electrode is situated on the side of said separator.

22. An electric double layer capacitor of claim 20, wherein said outside leading out electrodes are constituted with metal layers made by plasma spraying or arc spraying.

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FIG. 1

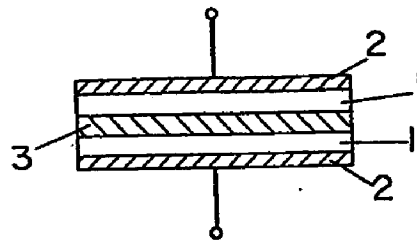


FIG. 2

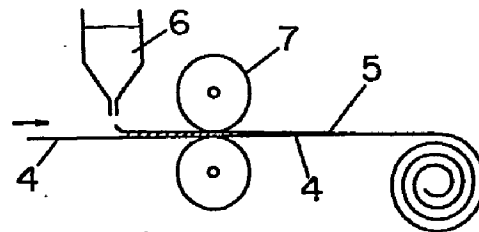


FIG. 3

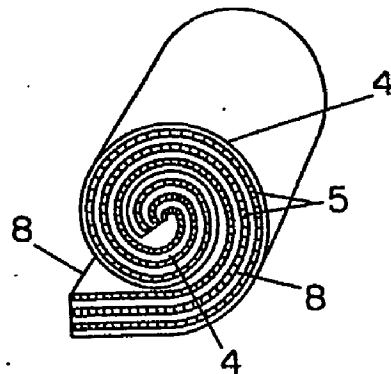


FIG. 4

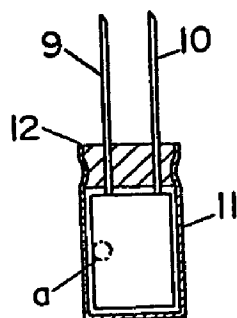


FIG. 5

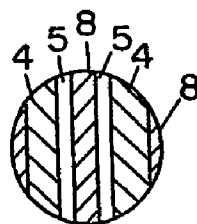


FIG. 6

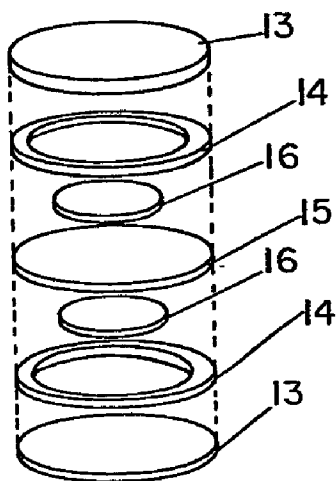


FIG. 7

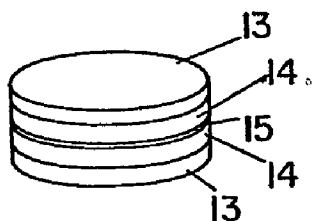


FIG.8

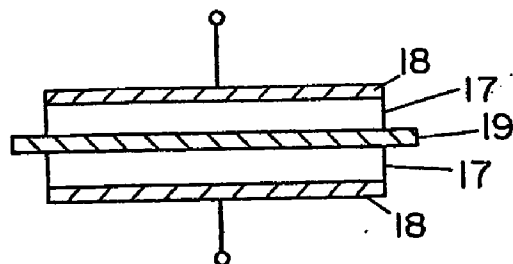


FIG.9

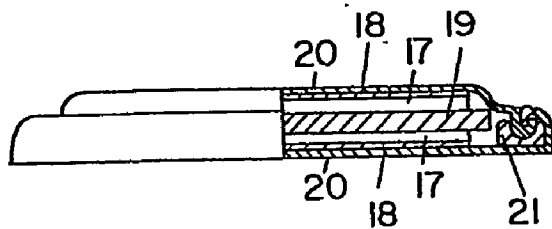


FIG. 10

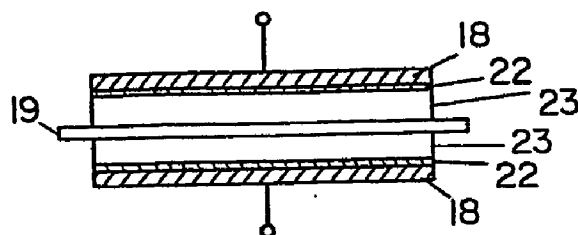


FIG. II

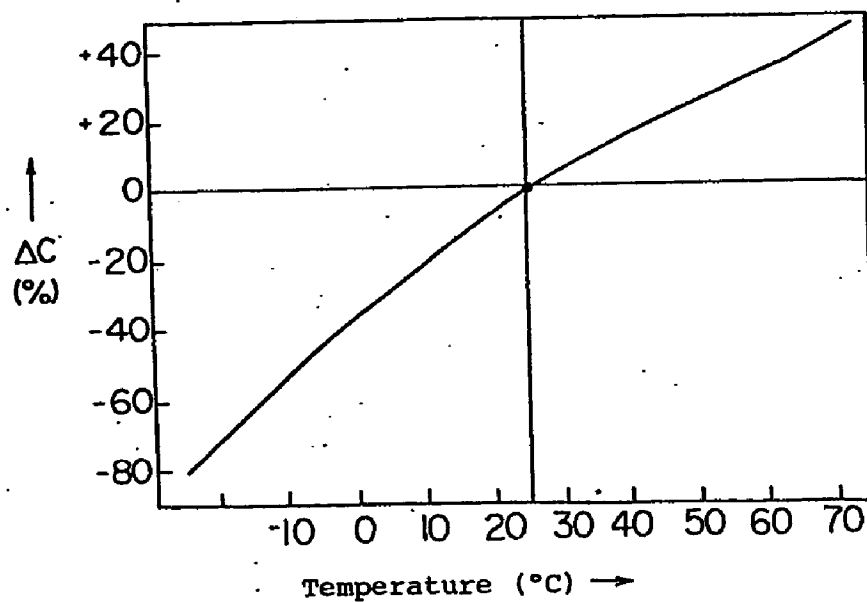


FIG. 12

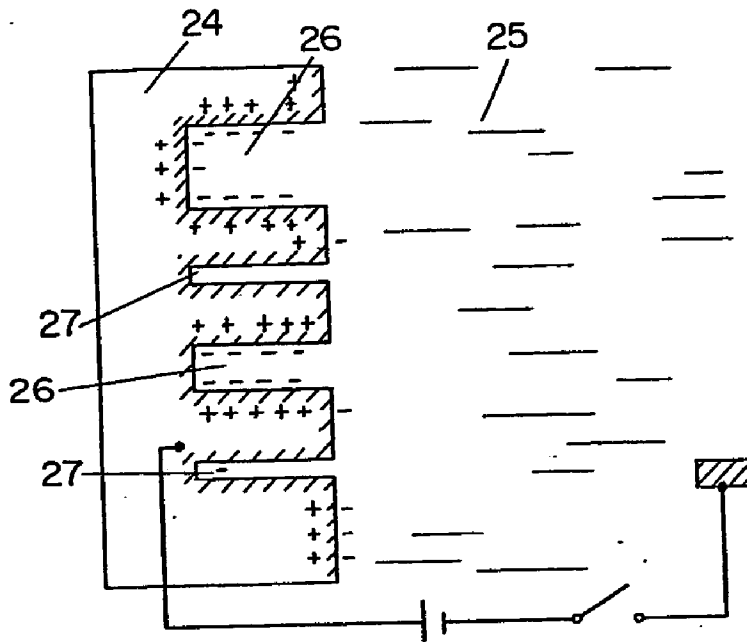


FIG. 13

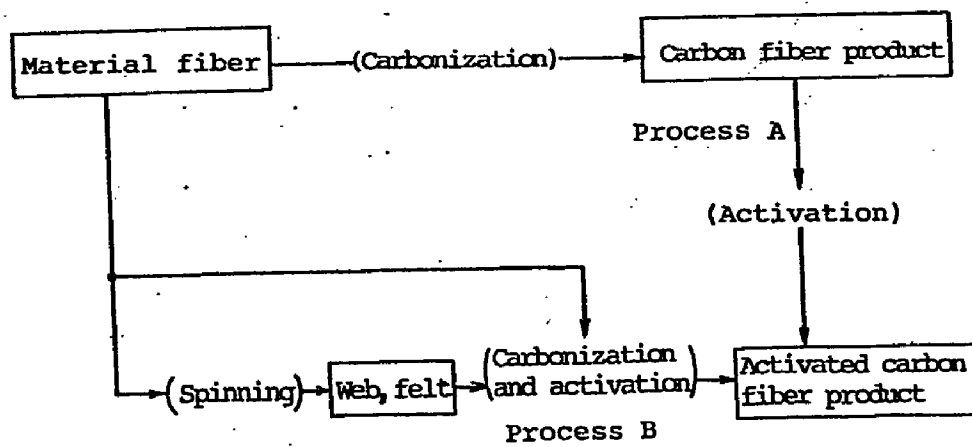


FIG. 14

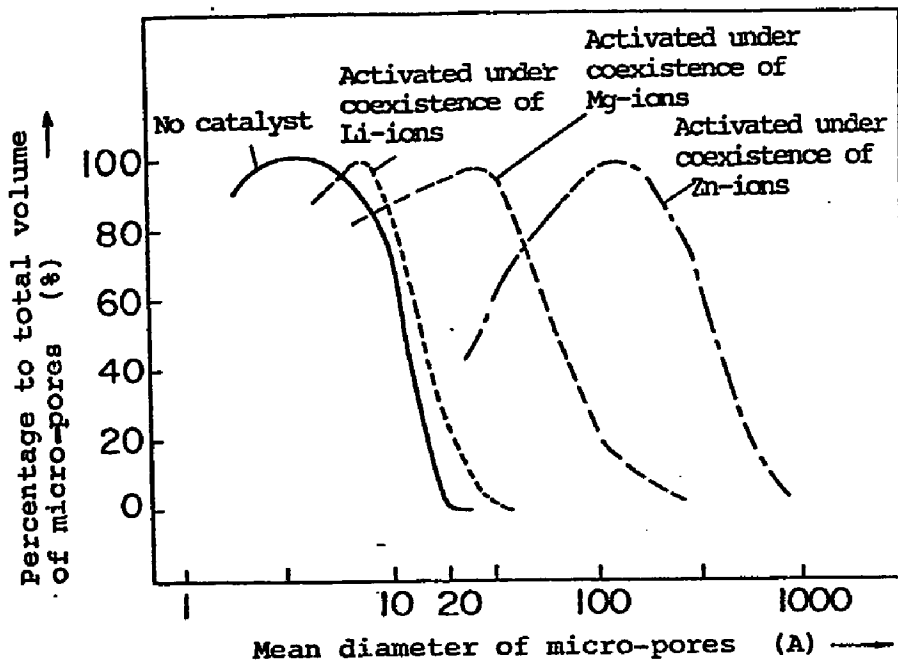


FIG. 15

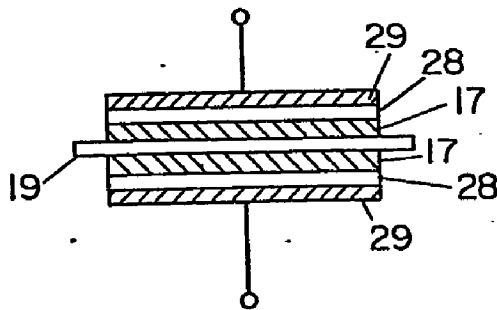


FIG. 16

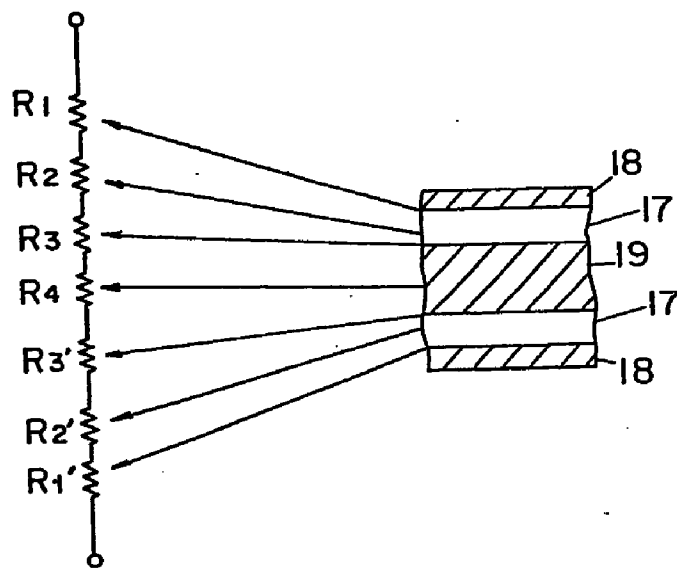


FIG.17

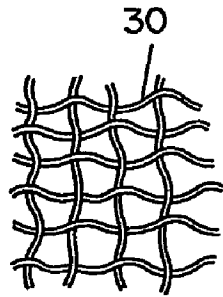


FIG.18

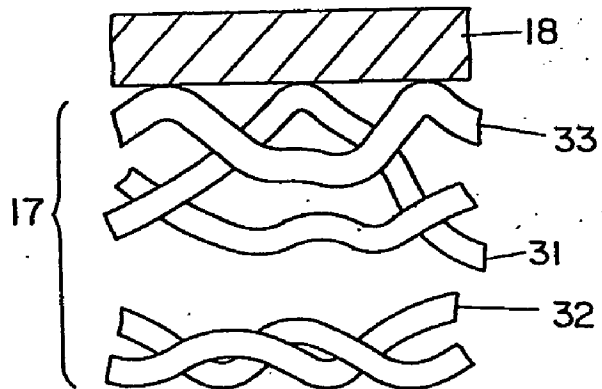


FIG. 19

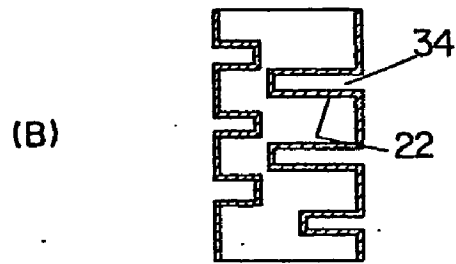
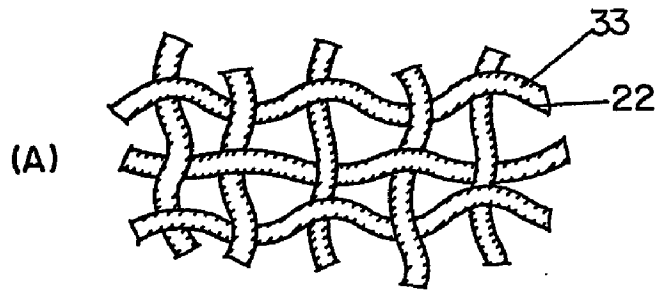


FIG. 20

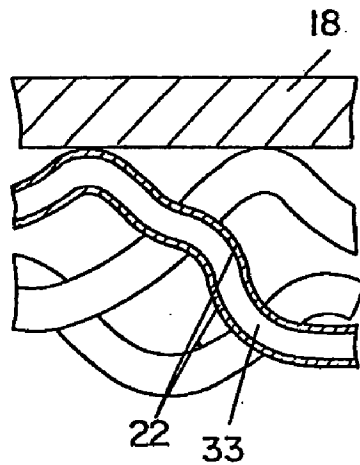
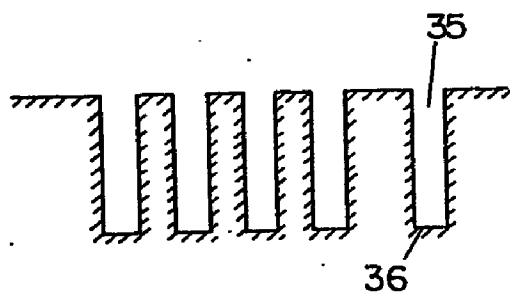


FIG. 21



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FIG. 22

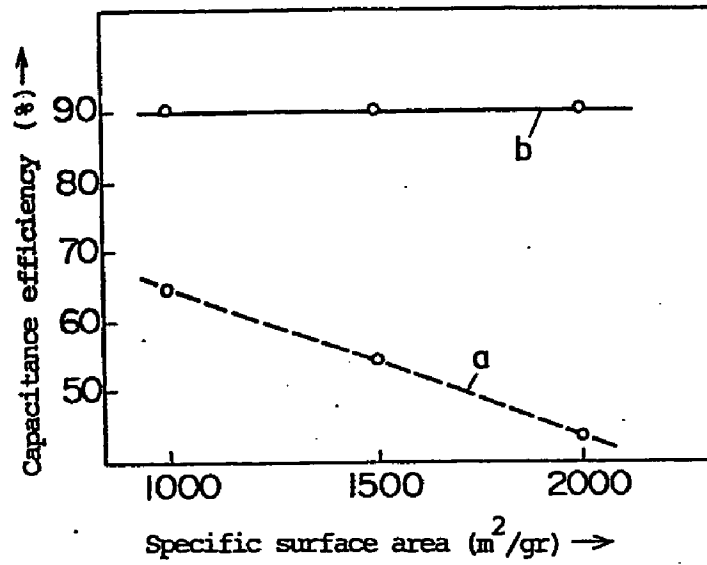
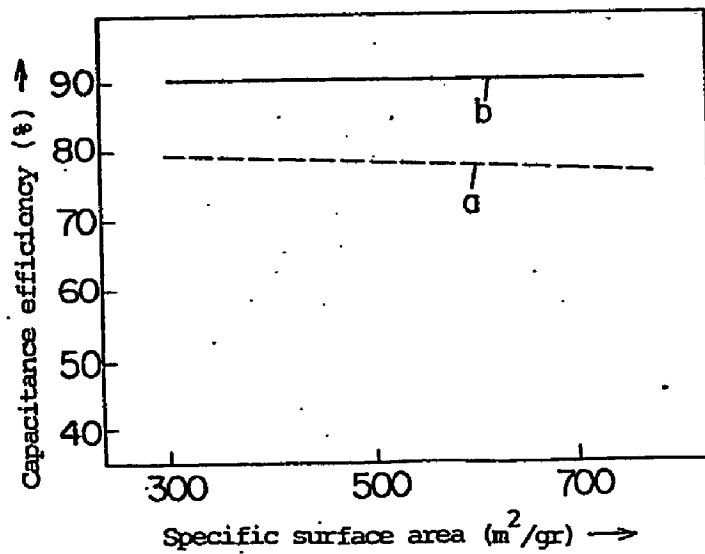


FIG. 23



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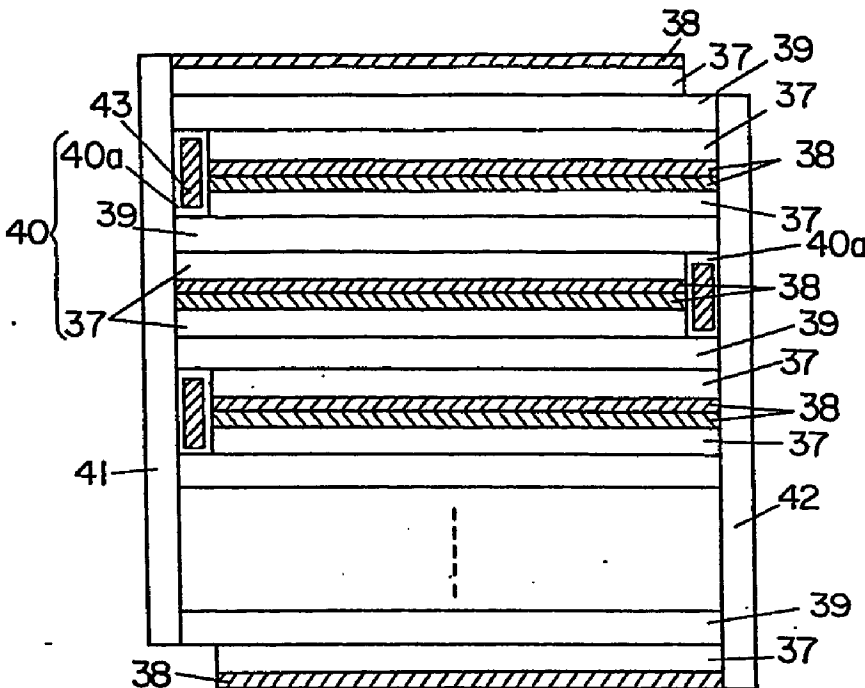


FIG. 25

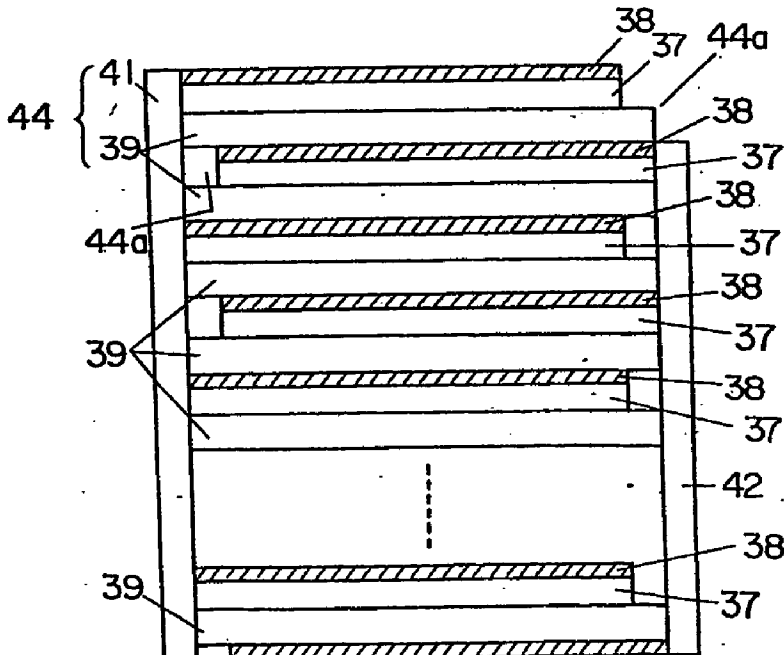


FIG. 26

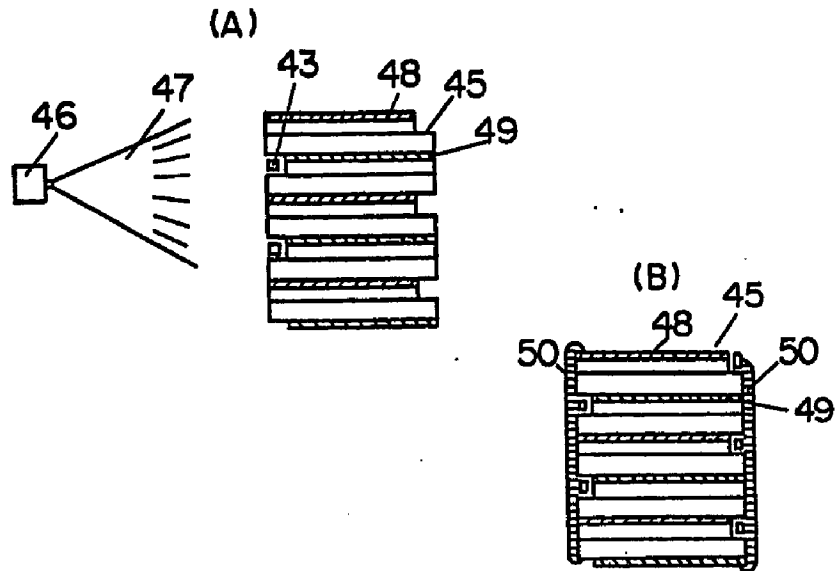


FIG. 27

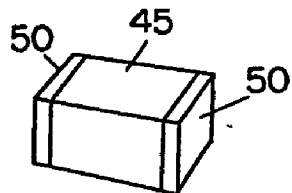


FIG. 28

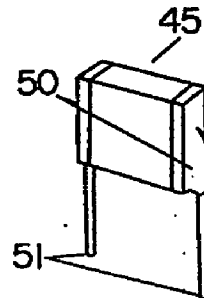


FIG. 29

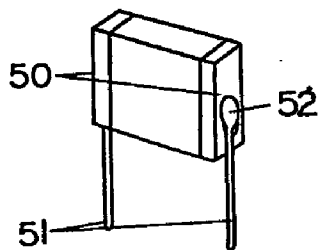


FIG. 30

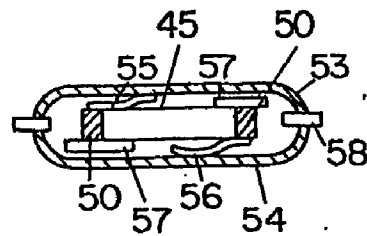


FIG. 31

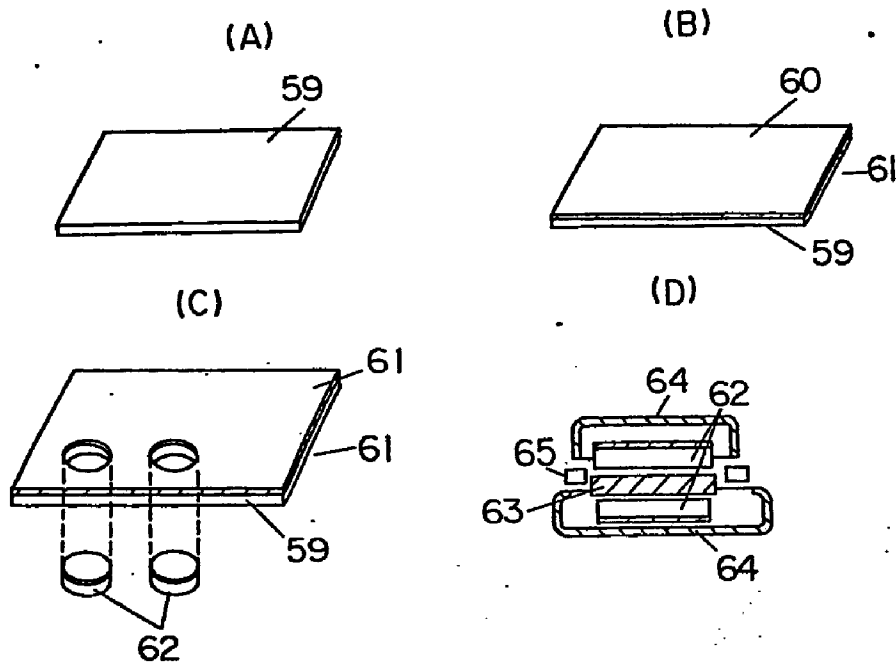


FIG. 32

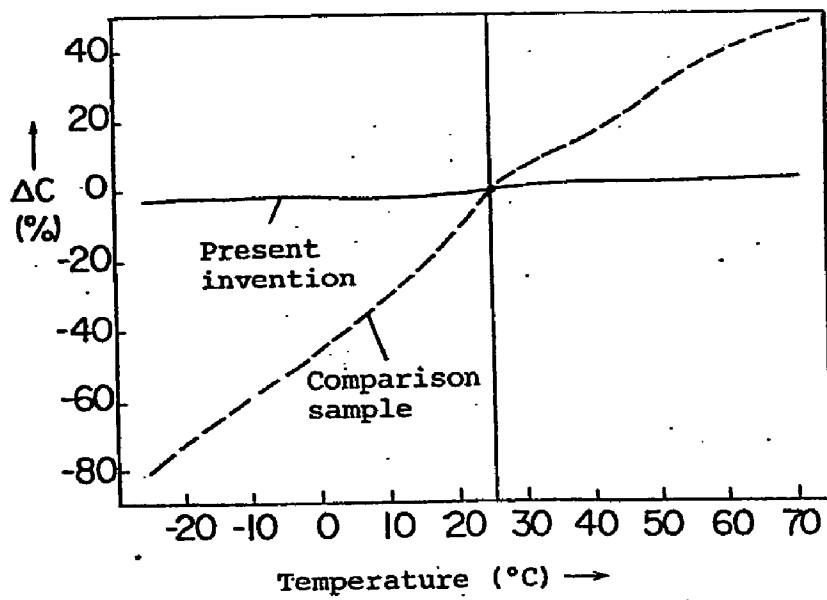


FIG. 33

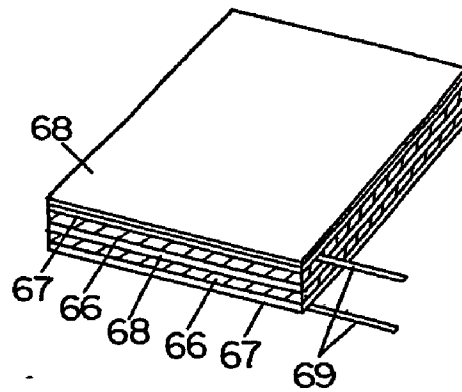
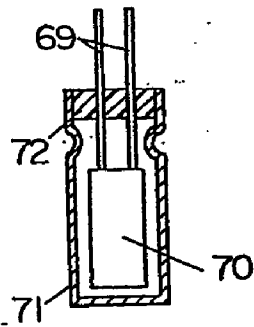


FIG. 34



0112929

List of the Reference Numerals of the Drawings

17, 37, 59 polarizable electrode
18, 38 conductive electrode
19, 39, 63, 68.. separator
20, 53, 54 metal case
21 insulative gasket ring
22 electric conductivity improving agent
23 activated carbon fiber
24 activated charcoal substrate
25, 32 electrolyte
26, 27, 35 micro-pores
28 conductive binder
29 metal foil
30, 33 activated carbon fibers
31 pore part
34 micro-pore part
36 bottom part
40, 44 unit capacitor element
40a, 44a margin part
41, 42 metal layer
43 spacer
45, 70 capacitor main body
46 plasma spray gun
47 metal powder
48, 49 electrode
50 sprayed electrode
51 metal lead wire
52 solder
55, 56 lead piece

57 insulation spacer
58, 65 gasket
60, 67 aluminium layer
61 double layer structure
62, 66 electrode
64, 71 case
69 lead wire
72 rubber cap

INTERNATIONAL SEARCH REPORT

0112923

International Application No. PCT/JP83/00208

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. ³ H01G 9/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
I P C	H01G 9/00	
✓	Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴	
	Kokai Jitsuyo Shinan Koho 1971 - 1982	
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁷	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹¹	Relevant to Claim No. ¹²
Y	JP,A, 55-99714 (Matsushita Electric Industrial Co., Ltd.), 30. July. 1980 (30. 07. 80)	1-11, 13, 14 16-18
Y	JP,U, 57-17136 (Nippon Condenser Kogyo Kabushiki Kaisha), 28. January. 1982 (28. 01. 82)	1-11, 13, 14 16-18
Y	JP,A, 57-12515 (Matsushita Electric Industrial Co., Ltd.), 22. January. 1982 (22. 01. 82) & EP,A1, 44427	1-11, 13, 14 16-18
Y	JP,A, 48-59363 (Western Electric Company, Inc.), 20. August. 1973 (20. 08. 73) & US,A, 3,700,975	13
A	JP,A, 55-99714 (Matsushita Electric Industrial Co., Ltd.), 30. July. 1980 (30. 07. 80)	12, 15 19-22
A	JP,A, 56-114312 (Nippon Condenser Kogyo Kabushiki Kaisha), 8. September. 1981 (08. 09. 81)	20-22
<p>¹ Special categories of cited documents: ¹¹</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
September 19, 1983 (19. 09.- 83)		September 26, 1983 (26. 09. 83)
International Searching Authority ¹		Signature of Authorized Officer ¹³
Japanese Patent Office		